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REPORT NO. 6
OF
PROGRESS ON INVESTIGATIONS OF CONFECTIONERY FATS
ANNUAL
Period Covered: June 1, 1960-June 1, 1961

Southern Utilization Research and Development Division
Oilseed Crops Laboratory
New Orleans, Louisiana

United States Department of Agriculture
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Report No. 6
of
Progress on Investigations of Confectionery Fats

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FOREWORD

This report describes the work of the research team composed of the Fellow of the National Confectioners Association, chemists of the Oilseed Crops Laboratory, engineers of the Engineering and Development Laboratory, and some members of the Spectroscopy Investigations. Each member of the team is in charge of or responsible for one or more phases of the work. Thus, the Fellow performed all of the laboratory work on the synthesis and characterization of the 1-oleodistearin and on the dilatometric examination of binary mixtures of the components of confectionery fats. He assisted in the dilatometric examination of Cocoa Butter-Like Fat No. 5 and cocoa butter. He carried out a large portion of the work toward determining the permeability of cocoa butter and Cocoa Butter-Like Fat No. 5 to water vapor. He assisted in the pilot plant and laboratory preparation of Cocoa Butter-Like Fat No. 5.

The research and development work described in this report is being carried out with the encouragement and support of the National

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Confectioners Association, its Research Advisory Committee, and the member firms of the Association. Thanks are expressed for their interest, encouragement and support.

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SUMMARY

Three experimental batches of cocoa butter-like fat were prepared in the laboratories and pilot plant of the Southern Utilization Research and Development Division. Two of these batches were combined, and the mixture (labeled Fat No. 5) is being evaluated by us and several members of the Research Advisory Committee. Analytical data have shown Fat No. 5 to have a melting range very similar to that of cocoa butter. Also, the fat tempers quickly and easily and should not present any problems of fat bloom. However, Fat No. 5 does not contract like cocoa butter on solidification and molding, and the gloss does not equal that of cocoa butter at its best.

The characterization of Fat No. 5 is continuing. One objective of this characterization is to find the handling procedures necessary for obtaining the best performance.

Cocoa Butter-Like Fat No. 5 was used by one confectioner to prepare an experimental batch of a chocolate-type coating composition. Also, a coating composition and a control made with cocoa butter were prepared in our laboratory. One or more of these compositions have been or are being evaluated by various individuals. Preliminary results indicate mouthing quality to be fairly satisfactory. However, there are differences between the coating compositions made with Fat No. 5 and that made with cocoa butter.

An investigation to establish quantitatively the effect of the various factors involved in the contraction of cocoa butter on molding and solidification is being made.

X-ray examinations of cocoa butter, Fat No. 5, and the individual components of these fats are being made to learn more about the behavior and proper handling of confectionery fats. X-ray diffraction spectra of both

cocoa butter and Fat No. 5 were too complex to readily relate changes in the spectra to changes in composition and thermal treatment. Therefore, most of the effort is being directed toward obtaining spectra of the individual components. Later these spectra will be used to analyze those of the two confectionery fats.

A pure sample of 1-oleodistearin, one of the major components of Fat No. 5, was synthesized in the laboratory, and a dilatometric examination was made. The expansivity of this component was found to be about 50% greater than that of a similar component (2-oleodistearin) in cocoa butter. Dilatometric data also have been obtained on binary mixtures of the important components of Fat No. 5 and cocoa butter. The data obtained indicate that the addition of the components of Fat No. 5 to those of cocoa butter speeds the rate of tempering and crystal transformation of the components of cocoa butter.

REPORT

A. Cocoa Butter-Like Fat

During the past year three batches of a cocoa butter-like fat were prepared in the pilot plant. In each of these preparations the starting materials were completely hydrogenated cottonseed oil and a refined, bleached and deodorized olive oil. The completely hydrogenated cottonseed oil was a commercial product of edible grade obtained from an oil processor. The olive oil, which was of domestic production, was obtained in the crude form and then refined, bleached, and deodorized in the laboratory.

In the pilot plant preparations 75 pounds of hydrogenated cottonseed oil was mixed with 25 pounds of the olive oil. The mixture was heated and dry nitrogen was bubbled through it for several hours to remove all traces of moisture and air. Then 0.2% of sodium ethoxide, prepared in the laboratory from ethyl alcohol and metallic sodium, was added as a rearrangement catalyst. The reaction was allowed to proceed for about 1.5 hr., after which the catalyst was destroyed by the addition of water and acetic acid. The reaction product then was mixed with water, allowed to settle, and the water layer was drawn off. This washing operation was repeated several times. Then the reaction product was dried by heating it and bubbling dry nitrogen through the melt.

The dry reaction product was dissolved in acetone (one part of product to four parts acetone, by weight), the solution was chilled to 63° F. to crystallize out of solution the unwanted, high-melting fraction, and the crystals and liquid were separated. The liquid portion was chilled further to 33° F. to obtain crystals of the cocoa butter-like fraction, which were removed from the residual solution. The

crystals of the cocoa butter-like fraction were spread out on trays and the acetone still adhering to the crystals was evaporated by passing a stream of air over the trays.

Unfortunately, the first batch of cocoa butter-like fat prepared in the pilot plant was unsatisfactory, the yield was low and the end product did not possess the anticipated characteristics. It was assumed that the interesterification step of the process did not proceed to the required degree.

Two additional pilot plant preparations were made as described above. In each the yield of cocoa butter-like fat was approximately 20%, based on the total weight of olive oil and completely hydrogenated cottonseed oil. The properties of these two batches of cocoa butter-like fat resembled those of Cocoa Butter-Like Fat No. 3, which was described in the last annual report. The two batches were combined for further experimental work.

Laboratory tests revealed that the new, composite lot of cocoa butter-like fat contained approximately 8% of components melting above 100° F. This percentage was enough to make the entire mixture slushy at 100° F.

Working with small portions from the composite lot of fat from the pilot plant, attempts were made to remove the portion melting above 100° F. In one experiment the fat was partially melted, cooled to 104° F. and held for 1 hr. Then an attempt was made to separate the solid and liquid portions by filtration. The initial rate of filtration was slow, and the rate decreased rapidly to an unsuitable level. Filtration at 100° F. could not be completed in a period of 11 hr. The yield after this time was only 32%. The fat crystals were too fine for removal by filtration.

In a second experiment the fat was melted by heating to 124° F. Then the temperature was decreased stepwise to 120°, 113°, and 106° F., the holding time at each temperature being about 1.5 hr. Subsequently, the temperature

was lowered to 100° F. and held at this level overnight (17.5 hr.). The following day the mixture was filtered at 100° F. Only about 3 hr. were required and the yield was 88.9%.

In a third experiment the fat was dissolved in petroleum ether (1 to 1 by weight), cooled to room temperature (about 70° F.), held overnight, and then filtered. The yield after removal of the petroleum ether from the filtrate was 94.6%.

This last mentioned procedure was deemed to be the best, and the bulk of the composite lot of fat from the pilot plant was treated in the same manner. The filtration was carried out at 68° F. and the yield was 93%.

The destearinized fat was steam deodorized in the laboratory for 1 hr. at 350° F. The finished product, which will hereafter be referred to as Cocoa Butter-Like Fat No. 5, was characterized in the laboratory. The iodine value was found to be 30.2. Melting point tests indicated that practically all of the fat melted just below 95° F., and the last trace of solids disappeared at about 122° F.

To obtain more complete data on melting characteristics, a dilatometric examination was made on a well-tempered sample of the fat. The contents of liquid oil calculated from these data are recorded in Table I. For comparison, data for Fat No. 3 and cocoa butter also are given.

From these data it is evident that insofar as melting characteristics are concerned, Cocoa Butter-Like Fat No. 5 should be equivalent to cocoa butter. The 3.7% of fat melting above 95° F. should not interfere with the mouthing quality of the product or with the workability at 95° F.

Table I. Liquid Content of Cocoa Butter-Like Fats and Cocoa Butter After Tempering

Temperature		Liquid content, %			
°C.	°F.	Cocoa butter	Fat No. 3	Fat No. 5	
0	32	0.6	2.1	...	
5	41	1.9	3.1	...	
10	50	4.1	3.6	...	
15	59	6.8	5.1	0.7	
20	68	10.8	10.6	8.1	
25	77	16.7	22.7	21.7	
30	86	36.1	40.3	46.7	
35	95	100.0	88.0	96.3	
40	104	...	96.0	96.9	
45	113	...	97.2	98.5	
50	122	...	100.0	100.0	

Samples of Fat No. 5 were sent to several members of the Research Advisory Committee. One of the members made a rather complete analysis of the fat and reported the following data:

Color (Lovibond scale)	35 yellow, 5.4 red
Free fatty acids (as oleic)	0.19%
A.O.M. stability (hours)	12.5
Unsaponifiabiles	0.49%
Flavor score	6.0
Solid fat index:	
50° F.	54.1
70° F.	59.5
92° F.	2.9
108° F.	2.4
Fatty acid composition:	
Lauric	0.2%
Myristic	0.4%
Palmitic	23.1%

Palmito-oleic	0.5%
Stearic	42.9%
Oleic	30.3%
Linoleic	2.6%
Saponification value	195.4
Softening point	97.7° F.
Capillary melting point	118.4° F.
Wiley melting point	105.1° F.
Iodine value	31.7

The best of the cocoa butter-like fats prepared heretofore possessed two undesirable characteristics: (1) the presence of a small percentage of high-melting solids, which made it difficult to use the fat under the usual enrobing conditions employed with confectionery coatings, and (2) the fat did not contract to the desired extent when solidified under the conditions used with cocoa butter.

To investigate the problem of mold release more fully, arrangements were made to have two, special, demountable molds machined from heavy aluminum plate. Using these molds and a cathetometer it was found possible to measure precisely the amount of linear contraction on molding and solidification. Attempts were made to find conditions under which Fat No. 5 would contract sufficiently for easy release from the mold. For example, it was thought that heating Fat No. 5 to well above its melting point, pouring it into the mold at this temperature, quickly solidifying the melt and chilling to 32° F., and then allowing the solid to slowly come to room temperature would cause the fat to contract through polymorphic transformation. Neither this procedure nor others produced the desired amount of

100	100
200	200
300	300
400	400
500	500
600	600
700	700
800	800
900	900
1000	1000
1100	1100
1200	1200
1300	1300
1400	1400
1500	1500
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3500	3500
3600	3600
3700	3700
3800	3800
3900	3900
4000	4000
4100	4100
4200	4200
4300	4300
4400	4400
4500	4500
4600	4600
4700	4700
4800	4800
4900	4900
5000	5000

The following table shows the results of the experiment. The first column shows the number of trials, and the second column shows the number of correct responses. The third column shows the percentage of correct responses. The fourth column shows the standard error of the mean. The fifth column shows the confidence interval. The sixth column shows the p-value. The seventh column shows the effect size. The eighth column shows the power of the test. The ninth column shows the significance level. The tenth column shows the test statistic. The eleventh column shows the critical value. The twelfth column shows the decision. The thirteenth column shows the conclusion. The fourteenth column shows the interpretation. The fifteenth column shows the summary. The sixteenth column shows the final result. The seventeenth column shows the overall conclusion. The eighteenth column shows the final statement. The nineteenth column shows the end of the document.

relatively rapid contraction. Under some operating procedures the fat contracted to a sufficient amount when allowed to remain in the mold for several hours. With aging the fat also acquired more brittleness and snap, but it never became as brittle as does cocoa butter.

Fat No. 5 had the desirable property of almost invariably solidifying to a solid of relatively good texture. Cocoa butter does not behave like this. In other words, the tendency to bloom was much less with Fat No. 5 than with cocoa butter. The best gloss obtainable with Fat No. 5 was not as good as the best gloss obtainable with cocoa butter.

We and others prepared several small batches of confectionery coatings with Fat No. 5. Our most recent confectionery coating composition was prepared according to the following formula:

Cocoa Butter-Like Fat No. 5	7.5 oz.
Lecithin	0.06 oz.
L. C. T. C. powder	17.1 oz.

The L. C. T. C. powder, obtained from a manufacturer of confectionery fats consisted of a micro-atomized mixture of cocoa powder, 11.6%; sugar, 76.5%; nonfat milk solids, 11.6%; and vanillin and salt. The lecithin and practically all of the fat were heated to 140-150° F. and the L. C. T. C. powder was added. Mixing at the same temperature was continued for one hour in a Hobart mixer operated at low speed. Then the mixture was cooled to 86° F. and, while mixing was continued, shavings of unmelted, tempered fat (equal to about 3% of the total fat) were added. The temperature was raised to 93° F., mixing was continued for an additional five to ten minutes, and the mixture was poured into a mold and chilled in a refrigerator at 40° F. for 20 minutes. Then the molded piece was stored at about 78° F.

Another sample was prepared in an identical manner, except that cocoa butter was used in place of Fat No. 5.

A portion of our supply of Fat No. 5 was sent to Mr. Norman Kempf, who arranged for a cooperating confectioner to incorporate it in an experimental coating composition. A portion of the coating composition was sent to us. A second portion was sent to another cooperating confectioner who used the composition in the preparation of several types of candy. In a letter of January 26, 1961, Mr. Kempf reported on the latter as follows:

"I visited Necco today, and inspected samples of candy prepared from a coating made from your Fat No. 5. A box containing some of these samples is being mailed to you directly from Necco. It contains the following:
Center- Shell molded candy with a toffee center.
One end- Bolster bars coated with this coating (naked)
Other end- Control Bolster bars coated with a commercial confectioners coating (Wrapped)

"You will note that the molded pieces contracted sufficiently to permit successful demolding, and have a good gloss. Normal chocolate tempering procedures would not work with this coating. In order to temper the coating for this shell work, it was cooled to 86 F. and then reheated to 100 F. and cast in the molds. This procedure resulted in contraction.

"You will also note that the coated Bolster bars have a very poor gloss. Necco's technicians have as yet been unable to work out a satisfactory tempering procedure for a coating method for bars of this kind, but the good gloss of the "back" of the shell molded pieces, indicates that it is possible to get a good gloss, and further work will undoubtedly result in working out a satisfactory tempering procedure.

"Further tests are under way to develop this tempering procedure, and to evaluate the shelf life of the test pieces."

Samples of all three coating compositions (the one prepared by the cooperating confectioner and the two prepared in our laboratory) were sent to another member of the Research Advisory Committee for taste panel evaluations. In the meantime other evaluations have been and are being made in our laboratory.

In our opinion each of the three coating compositions possessed good mouthing qualities. However, there were other differences. On comparing the two compositions made in our laboratory, that containing the cocoa butter was more brittle and had more snap immediately after molding and cooling at 40° F. The following day the two compositions were more alike in snap, but that made from cocoa butter still had more than that made with Fat No. 5. Both compositions released from the mold in this particular test, but that containing cocoa butter had shrunk the most. Also, that made with cocoa butter was darker in color and possessed more flavor and odor. Apparently the cocoa butter contained flavor components which complimented those in the cocoa powder.

Hardness vs. temperature data were determined for the three coating compositions. The hardness indices obtained (Table II) indicate that the composition containing the cocoa butter was much harder than those containing Fat No. 5.

Table II. Hardness Indices of the Confectionery Coatings

Temperature °F.	Coating Containing		
	Cocoa butter	Fat : No. 5 ^a /	Fat : No. 5 ^b /
67.3	94.5	34.8	25.8
75.7	47.7	22.6	15.2
82.0	21.4	11.1	12.5

^a/ Coating made by us.

^b/ Coating made by a confectioner.

A dilatometric examination was made of the two coatings prepared in our laboratory. As expected, when the coating containing Fat No. 5 was heated to a high temperature and then cooled rapidly, the fat solidified in low-melting forms but subsequently these transformed quite rapidly to the highest melting forms. On the other hand, the cocoa butter in the other coating composition solidified in quite stable, low-melting forms. In other words if Fat No. 5 is used in place of cocoa butter, the coating composition should offer much less of a problem in tempering and bloom.

B. Cost Analysis of the Process for Making Cocoa Butter-Like Fat

Members of the staff of the Engineering and Development Laboratory made a preliminary cost analysis of the preparation of cocoa butter-like fat by the currently used process. A copy of the analysis was distributed with one of the progress reports. Additional copies are available.

It should be emphasized that the costs which are cited are based on the pilot plant process presently in use and that this process places emphasis on the product rather than the method of preparation. For example, the reactants are stripped with dry nitrogen to ensure the removal of the last traces of moisture which might stop the interesterification reaction, and the reaction is carried out with an excess of catalyst. Somewhat similar interesterifications are carried out commercially after drying the reactants by a cheaper but less efficient method and using less catalyst. The costs given in the analysis probably can be reduced.

C. Experiments in Molding Cocoa Butter

As mentioned above, the failure of our cocoa butter-like fat to contract to the desired degree when solidified in molds is one of its faults. Cocoa butter apparently presents no great problem in this respect, though there appears to be no published information on the amount of contraction and no quantitative analysis of the factors involved. Such information should be useful. Therefore, a study of the contraction of cocoa butter on molding has been undertaken. In the course of this study the role of such factors as shrinkage caused by the change from the liquid to solid state, crystal size and arrangement, change in temperature, and polymorphic transformations will be considered.

In one series of tests cocoa butter was melted by warming and holding it at 95.0° F. Then samples measuring 25 x 7.5 x 3.3 mm. were solidified at various temperatures and the linear contractions were determined. At solidification temperatures of 57.2°, 60.8°, and 64.4° F. two-thirds or more of the total contraction was obtained within 10 minutes of the start of solidification. At 68.0° and 71.6° F. slower rates of contraction were found. Maximum contraction was found at temperatures of 60.8° F. and slightly lower, at which temperatures a linear contraction of about 2% was measured after 45 minutes. About four-fifths of this contraction occurred in the first 15 minutes.

When cocoa butter was heated to 116.6° F. and then solidified at 60.8° F. and maintained at this temperature for 5 hours, less than 0.5% contraction was found. On allowing this sample to come to room temperature, a sizable proportion melted, followed by slow resolidification to a spongy structure which showed no contraction.

Other experiments with cocoa butter were carried out using the specially machined aluminum molds. It was found that if partially melted cocoa butter has too high a solids content at the time of molding, contraction and appearance are poor. The point at which the solids content is too high is reached before the mixture becomes too stiff to pour. The best contraction and the most glossy appearance of the final solid were obtained when the cocoa butter was carefully and slowly heated to the point where the melt appeared to be clear to the eye (about 95° F.) and then poured into the mold and cooled rapidly to and held at 16° C.

Other experiments concerned with contraction during solidification are underway. With the aid of a special dilatometer it is hoped to correlate linear contraction in molds with total volumetric contraction. X-ray experiments also will be made of samples after various temperature treatments and the role of polymorphism, which is believed to be of major importance, will be established.

In another phase of the investigation of cocoa butter the temperature at which fixed proportions of a well-seeded, well-tempered sample of cocoa butter melted after various storage intervals was determined. The data obtained are recorded in Table III.

Table III. Changes in Melting Characteristics of Well-Tempered Cocoa Butter on Storage at 77° F.

Storage time at 77° F.	Temperature at which sample was melted to the indicated amount			
	20%	50%	80%	100%
16 Hours	78.8	84.0	88.2	--
2.5 Days	--	86.5	90.0	94.1
8 Weeks	85.6	89.2	91.8	95.9

Other investigators have come to the conclusion that a well-tempered sample of cocoa butter will change into the highest melting crystal form when held at room temperature for perhaps 0.5 hour. Some of our data tend to confirm this. Yet, small changes in the point of complete melting did occur with the passage of time, and the melting range tended to become shorter. Possibly changes in crystal size or changes in the number and types of phases present may be responsible. The experiments will be repeated and X-ray diffraction patterns will be obtained in an attempt to find an explanation of the observed behavior.

D. Permeability to Moisture

The permeability to moisture of several films of cocoa butter and Fat No. 5 is being measured. The films were solidified and treated in different manners. Thus far the lowest permeability was obtained with a film of cocoa butter. This film was made by carefully melting the cocoa butter at 94.1° F. and then solidifying the film by rapid cooling to 61° F. and keeping it at this temperature for one hour. This film was stored at 77° F. for 50 hours before the permeability measurements were begun. The permeability constant measured at room temperature over a two-week period was 5×10^{-12} . The permeability constant was measured as described in our article in the Journal of the American Oil Chemists' Society, volume 37, pages 1-4, 1960. The index found in the current tests is about one-sixth of those reported previously.

A second film of cocoa butter was prepared by a procedure similar to that described above except that the film was solidified at 68° F. This second film had a permeability constant of about 6×10^{-12} .

Two films of Cocoa Butter-Like Fat No. 5 were prepared and tested. In one case the fat was melted by heating to 122° F. and in the other it was cooled to 93° F. and seeded, and held at this temperature for 1.5 hours. Both films were solidified at 61° F., held for one hour at 61° F., and then for 16 hours at 77° F. Both films had a permeability constant of 24×10^{-12} on testing for 6 to 10 days. Apparently Fat No. 5 is more permeable to water vapor than is cocoa butter but its permeability is relatively insensitive to variations in melting and solidification.

E. Slab Oils

No additional work on slab oils was performed during the current reporting period. Several additional samples of the mixture of

dibutyropalmitins and dibutyrostearins prepared previously were sent to individuals who expressed an interest in them.

During the current reporting period an event occurred which should be of interest to confectioners who use slab oils, gloss oils, and waxes. Largely through the efforts of Distillation Products Industries,^{1/} Rochester, New York, approval for the use of acetoglycerides on and with foods was obtained from the Food and Drug Administration. The acetoglycerides may now be used at levels up to 5%.

The acetoglycerides, which are modified fats, form a series of products ranging from liquid oils possessing exceptional resistance to rancidity to fats which are nongreasy, plastic solids. The unique properties of the compounds were first described in 1952 in an article prepared at the Southern Regional Research Laboratory. Since that time numerous articles describing additional research have been published. Also, in a letter of understanding with Distillation Products Industries arrangements were made for cooperative work. The company's interest in the acetoglycerides continued and through the efforts of this company approval has been obtained from the Food and Drug Administration to use the acetoglycerides in cosmetics and on and with foods. Approval for the latter uses was given on July 20, 1960. The company has issued a number of data sheets describing the products and technical bulletins (A-1 through A-7) suggesting potential uses. Bulletin A-6 is entitled "Edible Protective Coatings of Nuts and Confections with MYVACET Distilled Acetylated Monoglycerides."

^{1/} It is not the policy of the Department to recommend or endorse the products of any one particular company. The name of the company is supplied merely as a matter of information.

F. X-Ray Examinations

A sample of Cocoa Butter-Like Fat No. 5 was sent to a processor of fats and oils for X-ray examination. A report has not yet been received.

An X-ray examination of Fat No. 5 and cocoa butter after various temperature treatments also has been undertaken by a cooperating group in our Laboratory. A new, recently installed General Electric XR-D5 instrument is being used in this work. With it a sample can be scanned over a two theta angle of 40° to 0° in 20 minutes. The entire diffraction spectrum is automatically recorded. Formerly the equivalent of these operations required several hours for each sample. A special cold stage has been installed on the instrument to make possible the control of the temperature of the sample. Also, if desired, the temperature can be lowered to a level at which polymorphic transformations are virtually halted.

So far the experimental work has been concerned mostly with determining the best operating conditions, including both instrument settings and manipulation of the samples. The spectra of well-tempered samples of both Fat No. 5 and cocoa butter have been found to be reproducible, but the spectra of samples of both Fat No. 5 and cocoa butter solidified by quick chilling have not been reproduced in exact detail. Small, uncontrolled variations in the solidification techniques apparently produced detectable changes in the types and proportions of the various polymorphs in the samples. Some spectra were practically identical except for unexplained shifts in the relative positions of the entire spectra, which produced systematic differences in the calculated crystal spacings of the samples.

The spectrum of a well-tempered sample of Fat No. 5 resembles those of quick-chilled samples of Fat No. 5 and cocoa butter more closely than it does that of well-tempered cocoa butter, which is undoubtedly a reflection of the large proportions of the 2-oleo-glycerides present in Fat No. 5. These glycerides are thermodynamically stable in the beta prime form, while the 1-oleo-glycerides of cocoa butter are unstable in this form.

Because of the complexity of the spectra of cocoa butter and Fat No. 5, work was started toward obtaining an X-ray diffraction spectrum of each of the polymorphic forms of the major components of confectionery fats. By superimposing these spectra it is hoped that the changes in the spectra of confectionery fats can be interpreted more precisely. This also should make possible the determination of the types and proportions of the crystal forms present in confectionery fats which have been tempered and solidified in a given manner.

G. Characterization of Individual Components of Confectionery Fats

As mentioned in other reports, our cocoa butter-like fats are composed in part of the same triglycerides, or fatty components, found in cocoa butter, and in addition contain some closely related triglycerides referred to technically as positional isomers. One of the latter is 1-oleodistearin, the positional isomer of 2-oleodistearin.

A sample of 1-oleodistearin which was synthesized in the laboratory and purified to a high degree, was examined. The 1-oleodistearin was found to possess two distinct melting points, 86.7° F. and 107.8° F. Dilatometric

examination gave evidence that some types of thermal treatment cause the melt to solidify to an amorphous glass rather than solidify into a crystalline structure. This behavior had heretofore not been discovered among the components of natural fats or fats derived from them by hydrogenation, though we have observed a similar behavior with some modified fats. Additional work is required to verify the conclusion that 1-oleodistearin solidifies to an amorphous glass.

Dilatometric curves for the two polymorphs of 1-oleodistearin were obtained and melting dilations and expansivities were calculated. The melting dilation of the highest melting polymorph or Form I was calculated to be 11.1% at its melting point of 107.8° F. This dilation is almost exactly equal to that of its positional isomer, 2-oleodistearin, which is one of the major components of cocoa butter. However, the expansivity of the highest melting form of 1-oleodistearin, which was calculated to be 0.025% per degree Fahrenheit, is about 50% greater than that of 2-oleodistearin. The 1-oleodistearin was found to be a peculiar compound in that the lower melting polymorph existed in two modifications, and the transformation from one to the other was reversible, the change occurring at about 32° F. X-ray examination confirmed this peculiarity.

To obtain basic information on the compatibility of the components of Cocoa Butter-Like Fat No. 5 and cocoa butter, dilatometric examinations were made of mixtures of 1-oleopalmitostearin with 2-oleopalmitostearin and of 1-oleodistearin with 2-oleodistearin.

A 1:1 mixture of 1-oleopalmitostearin and 2-oleopalmitostearin was examined. This mixture on being quickly solidified and then held overnight

at 77° F. exhibited a broad melting range with the midpoint occurring at about 80.6° F. Somewhat independent melting of the individual components and polymorphic forms seemed to occur. After being well-tempered, the mixture possessed a melting range which was definitely longer than that of mixtures of 2-oleopalmitostearin and 2-oleodistearin examined earlier. The latter compounds, which are the major components of cocoa butter, yielded mixtures which behaved somewhat like single compounds. The well-tempered mixture of 1-oleopalmitostearin and 2-oleopalmitostearin exhibited an expansivity of 0.021% per degree Fahrenheit and a melting dilation of 10.3% measured at the point of complete melting.

Dilatometric measurements were made on a mixture of 27.8% 2-oleodistearin and 72.2% 1-oleodistearin. This proportion was selected to facilitate comparison with a mixture of 2-oleopalmitostearin and 2-oleodistearin examined previously. Under conditions of slow solidification the present mixture exhibited slight breaks in the melting portion of the curves, indicating that individual melting of the components tended to occur. Expansivity in the solid state was 0.027% per degree Fahrenheit for a well-tempered sample, and melting dilation was 9.4%.

After a comparison of the rates of polymorphic transformation in the mixtures which were currently investigated with those investigated previously, it was concluded that the mixing of two glycerides which exhibit widely different rates of polymorphic transformation may actually serve to increase the rate of transformation of the slower one. Possibly the more easily transformed component can serve as "seed" for the other.



